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A continuous time random walk approach to the stream transport of solutes

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[1] The transport of solutes in rivers is influenced by the exchange of water between the river and the underlying hyporheic zone. The residence times of solutes in the hyporheic zone are typically much longer than traveltimes in the stream, resulting in a significant delay in the downstream propagation of solutes. A new model for this process is proposed here on the basis of the continuous time random walk (CTRW) approach. The CTRW is a generalization of the classic random walk that can include arbitrary distributions of waiting times, and it is particularly suited to deal with the long residence times arising from hyporheic exchange. Inclusion of suitable hyporheic residence time distributions in the CTRW leads to a generalized advection-dispersion equation for in-stream concentration breakthrough curves that includes the effects of specific hyporheic exchange processes. Here examples are presented for advective hyporheic exchange resulting from regular and irregular series of bedforms. A second major advantage of the CTRW approach is that the combined effects of different processes affecting overall downstream transport can be incorporated in the model by convolving separate waiting time distributions for each relevant process. The utility of this approach is illustrated by analyzing the effects of local-scale sediment heterogeneity on bedform-induced hyporheic exchange. The ability to handle arbitrarily wide residence time distributions and the ability to assess the combined effects of multiple transport processes makes the CTRW model framework very useful for the study of solute transport problems in rivers. The model presented here can be easily extended to represent different types of surface-subsurface exchange processes and the transport of both conservative and nonconservative substances in rivers.

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1. Introduction

[2] In his seminal work, *Taylor* [1954] gave a mathematical description of the basic processes that govern the transport of dissolved substances in flowing fluids. The core of Taylor's work lies in the fundamental concept of shear dispersion, which involves mixing due to spatial variability in the flow field. This process produces a progressive spreading of dissolved and suspended substances that causes the variance of the concentration distribution to increase with time. More precisely, Taylor showed that, after a sufficient mixing distance, the variance grows linearly and the concentration distribution then follows Fick's law of diffusion

$$q = -K\nabla C, \tag{1}$$

where q is the mass flux per unit area, K is the dispersion coefficient, and C is the average concentration over the cross section. Taylor's model for longitudinal solute transport is commonly referred to as the advection-dispersion equation (ADE). For the case of a uniform stream cross section, this can be written as

$$\frac{\partial C}{\partial t} + U\frac{\partial C}{\partial x} = K\frac{\partial^2 C}{\partial x^2}, \tag{2}$$

where t is time, x is the longitudinal position, and U is the average velocity over the cross section. The ADE has routinely been employed for the study of dispersion problems in rivers [e.g., *Yotsukura et al.*, 1970; *Fischer et al.*, 1979; *Schnoor*, 1996, and citations therein].

[3] When classical theory for shear dispersion has been applied to rivers, the river bed has normally been assumed to be impermeable. However, numerous observations have demonstrated that there is substantial water flux across stream channel boundaries [e.g., *Bencala and Walters*, 1983; *Thibodeaux and Boyle*, 1987; *Harvey and Wagner*, 2000; *Packman and Bencala*, 2000], and the resulting transport of dissolved solutes and suspended particles plays an important role in riverine ecosystems [e.g., *Brunke and Gonser*, 1997; *Boulton et al.*, 1998; *Jones and Mulholland*,

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2000; *Hancock et al.*, 2005]. The velocity field in this flow continuum (including subsurface pore water) is far less uniform than what has been previously assumed in applying Taylor dispersion theory to rivers, and this wide range of velocities plays an important role in the stream transport of solutes. The exchange with the hyporheic zone has been shown to produce a consistent delay in solute transport relative to the mainstream flow, leading to long tails (high skewness) in time concentration breakthrough curves (BTCs) for downstream transport [*Nordin and Troutman*, 1980; *Bencala and Walters*, 1983; *Schmid*, 2002; *Wörman et al.*, 2002].

[4] Various models have been proposed to reproduce the non-Fickian behavior observed in the data. The most commonly used formulation is the transient storage model (TSM) proposed by *Bencala and Walters* [1983], which idealizes the flow continuum as a two-layer system and represents exchange between the surface and subsurface flows in terms of a mass transfer coefficient,

$$\frac{\partial C}{\partial t} + U\frac{\partial C}{\partial x} = K\frac{\partial^2 C}{\partial x^2} + \alpha(C_S - C) \tag{3}$$

$$\frac{\partial C_S}{\partial t} = \alpha\frac{A}{A_S}(C - C_S), \tag{4}$$

where C is now the concentration in the mainstream, C_S is the concentration in the storage zone, α is a mass transfer coefficient with units of inverse time, and A/A_S is the ratio between the cross-sectional area of the stream and the storage zone area. The TSM has been widely applied to infer both in-stream and hyporheic transport properties by fitting the results of solute injection experiments [e.g., *Broshears et al.*, 1993; *Harvey et al.*, 1996; *Harvey and Fuller*, 1998; *Fernald et al.*, 2001; *Thomas et al.*, 2003]. While this model often provides an adequate description of in-stream solute concentration data over a limited range of timescales, it has been shown to generally underestimate the slower exchange that occurs with deeper or longer hyporheic flow paths [*Wörman et al.*, 2002; *Marion et al.*, 2003; *Zaramella et al.*, 2003]. Essentially, the first-order mass transfer term in (3)–(4) assumes that the subsurface is a well-mixed reservoir, while in reality hyporheic exchange is generally characterized by strong spatial variations in the subsurface [*Marion and Zaramella*, 2005a]. Therefore, while the TSM still represents a practical tool for assessing non-Fickian behavior in downstream solute transport, its mathematical structure prevents it from providing a comprehensive description of the hyporheic exchange process. Models with a structure similar to the TSM [e.g., *Castro and Hornberger*, 1991; *Hart*, 1995] also have similar limitations in the description of the hyporheic exchange.

[5] More recently, efforts have been made to include a wider range of exchange timescales in non-Fickian solute transport models for rivers [*Haggerty et al.*, 2000, 2002; *Wörman et al.*, 2002; *Marion and Zaramella*, 2005b]. The mathematical structure of these models is similar to the TSM but allows inclusion of various forms of the hyporheic residence time distribution. That is,

$$\frac{\partial C}{\partial t} + U\frac{\partial C}{\partial x} - K\frac{\partial^2 C}{\partial x^2} = J_s, \tag{5}$$

where the solute exchange flux, J_s, is explicitly related to the water flux across the boundary, q, and the distribution of solute residence times in the subsurface, $f(T)$. This approach gives rise to a convolution integral for the time history of in-stream solute concentrations in terms of the hyporheic residence time distribution [*Elliott and Brooks*, 1997]. The most noteworthy feature of this type of approach is that it can theoretically encompass any form of $f(T)$, whereas the TSM and related model frameworks implicitly assume an exponential residence time distribution. Therefore this approach essentially represents a generalization of the TSM that allows a variety of hyporheic exchange processes to be explicitly modeled by means of appropriate formulations for q and $f(T)$. For example, this type of model has been employed with a physically based residence time distribution for advective hyporheic exchange induced by bedforms, and was shown to provide a much more realistic description of the time history of solute concentrations in the subsurface than the TSM [*Wörman et al.*, 2002].

[6] Here we present an improved theoretical and practical modeling approach for analysis of solute transport in rivers based on continuous time random walk (CTRW) theory [*Montroll and Weiss*, 1965; *Scher and Lax*, 1973]. This approach has been recently applied to the transport of both conservative and nonconservative substances in groundwater, and has been shown to provide a parsimonious description of the anomalous (non-Fickian) transport behavior that occurs because of structural heterogeneities in porous media [*Berkowitz et al.*, 2006; *Cortis et al.*, 2006]. Our application to the case of rivers is conceptually similar to the approaches of *Wörman et al.* [2002], *Haggerty et al.* [2000, 2002], but it presents a number of advantages. First, the CTRW approach does not require explicitly modeling the mass balance between the surface and subsurface, as it is based on a single equation for net downstream transport that can include the effects of the full range of velocities found in the flow continuum. This is conceptually important because it avoids the artificial separation of the problem at the stream channel boundary. Quantitatively, this approach is favorable because it provides a parsimonious description of the transport behavior, as opposed to the overparameterization that typically results from independent representation of in-stream and subsurface mixing behavior. Secondly, the CTRW approach provides a clear and well-defined framework for representing the multiple scales of transport found in heterogeneous and dynamic river systems, i.e., variability in stream flow, patterns of hyporheic exchange, and heterogeneity in sediment properties. Therefore this approach can readily be used to investigate the combined effects of different transport processes over a wide range of spatial and temporal scales.

2. Model

2.1. CTRW Theory

[7] The classical ADE can be obtained from conventional random walk theory [see, e.g., *Fischer et al.*, 1979]. In this conceptual framework, mixing is envisioned as a sequence of displacements of constant lengths that occur in random directions and at regular time intervals, and the ADE arises from the ensemble average over many individual transport events. The symmetric concentration curves that are found

from the ADE are essentially an outcome of the central limit theorem when the transport behavior is averaged over travel distances and times that are long relative to the scale of the random walk. The difficulty presented by hyporheic exchange is that the exchange timescale can be so long that the requisite averaging implicit in the ADE may not occur. In this case, the resulting concentration curves will be asymmetric, and sometimes strongly so, as described by *Fischer et al.* [1979, p. 131]. This behavior can be represented by a generalization of the random walk process, namely the continuous time random walk (CTRW), which leads to a new transport equation that includes the anomalous features shown by the concentration breakthrough curves [*Berkowitz et al.*, 2006].

[8] Let us consider a particle that moves with a sequence of random jumps with different lengths and durations. For the sake of simplicity, a one-dimensional domain is considered. The length and duration of the particle jumps are treated as random variables with a joint pdf $\Psi(x, t)$, whose marginal distributions are $\lambda(x)$ and $\psi(t)$, respectively.

[9] An equation for the evolution of the particle position is now derived. The following relationship holds:

$$p(x,t) = \int_0^t \omega(t-\tau)R(x,\tau)\mathrm{d}\tau, \tag{6}$$

where $p(x, t)$ is the probability for a particle be found at position x at time t, $R(x, t)$ is the probability for the particle to be just arrived at the point x at time t, and

$$\omega(t) = 1 - \int_0^t \psi(\tau)\mathrm{d}\tau \tag{7}$$

is the probability for a particle of not making a jump during the interval t. Equation (6) simply states that a particle can be found at x at time t if it arrived there at τ and did not jump away during the interval $t - \tau$.

[10] The starting point of this analysis is the probability for a particle to be just arrived at the point x at time t after $n + 1$ jumps, which can be written as

$$R_{n+1}(x,t) = \int_0^t \int_{-\infty}^{+\infty} \Psi(x-x', t-t')R_n(x',t')\mathrm{d}x'\mathrm{d}t', \tag{8}$$

where the relationship between R and R_n is simply

$$R(x,t) = \sum_{n=0}^{\infty} R_n(x,t). \tag{9}$$

It is important to stress that the convolution integral over t' in equation (8) allows for the possibility of very long times to occur between consecutive particle jumps. Similarly, the integral over x' includes the possibility of particles making very long jumps. This is significant because long holding times and jump lengths both tend to favor anomalous transport behavior.

[11] Without loss of generality, it can now be assumed that the initial position of the particle at the instant $t = 0$ is $x = 0$, that is, $R_0(x, t) = \delta(x)\delta(t)$. If the sum operator $\Sigma_{n=0}^{\infty}$ is applied to equation (8), it becomes

$$R(x,t) - \delta(x)\delta(t) = \int_0^t \int_{-\infty}^{+\infty} \Psi(x-x', t-t')R(x',t')\mathrm{d}x'\mathrm{d}t' \tag{10}$$

or, recalling the definition of the Laplace transform, $\tilde{f}(u) = \int_0^{+\infty} f(t)\mathrm{e}^{-ut}\mathrm{d}t$,

$$\tilde{R}(x,u) - \delta(x) = \int_{-\infty}^{+\infty} \tilde{\Psi}(x-x',u)\tilde{R}(x',u)\mathrm{d}x'. \tag{11}$$

[12] It is now possible to relate the equation in $R(x, t)$ to the desired statistical description of particle motion, $p(x, t)$. The Laplace transform of (6) can be written as

$$\tilde{R}(x,u) = \frac{u}{1-\tilde{\psi}(u)}\tilde{p}(x,u). \tag{12}$$

This expression can be introduced in equation (11), thus obtaining

$$\frac{u}{1-\tilde{\psi}(u)}\tilde{p}(x,u) - \delta(x) = \int_{-\infty}^{+\infty} \frac{u\tilde{\Psi}(x-x',u)}{1-\tilde{\psi}(u)}\tilde{p}(x',u)\mathrm{d}x' \tag{13}$$

and, after subtracting $u\tilde{\psi}(u)\tilde{p}(x, u)/(1 - \tilde{\psi}(u))$,

$$u\tilde{p}(x,u) - \delta(x) = \int_{-\infty}^{+\infty} \frac{u\tilde{\Psi}(x-x',u)}{1-\tilde{\psi}(u)}\tilde{p}(x',u)\mathrm{d}x' - \frac{u\tilde{\psi}(u)}{1-\tilde{\psi}(u)}\tilde{p}(x,u). \tag{14}$$

[13] If now we make use of the identity

$$\tilde{\psi}(u) = \int_{-\infty}^{+\infty} \tilde{\Psi}(x'-x,u)\mathrm{d}x', \tag{15}$$

it is then possible to write equation (14) as

$$u\tilde{p}(x,u) - \delta(x) = \int_{-\infty}^{+\infty} \frac{u\tilde{\Psi}(x-x',u)}{1-\tilde{\psi}(u)}\tilde{p}(x',u)\mathrm{d}x' - \int_{-\infty}^{+\infty} \frac{u\tilde{\Psi}(x'-x,u)}{1-\tilde{\psi}(u)}\tilde{p}(x,u)\mathrm{d}x' \tag{16}$$

or, after the application of the inverse Laplace transform,

$$\frac{\partial p(x,t)}{\partial t} = \int_{-\infty}^{+\infty} \int_0^t \Phi(x-x',t-t')p(x',t')\mathrm{d}x'\mathrm{d}t' - \int_{-\infty}^{+\infty} \int_0^t \Phi(x'-x,t-t')p(x,t')\mathrm{d}x'\mathrm{d}t' \tag{17}$$

where

$$\tilde{\Phi}(x,u) = \frac{u\tilde{\Psi}(x,u)}{1-\tilde{\psi}(u)}. \tag{18}$$

[14] Equation (17) is known as the generalized master equation (GME) [*Klafter and Silbey*, 1980], and it describes the evolution in time of the particle distribution $p(x, t)$. When the particles represent a dissolved tracer moving in a stream, the pdf $p(x, t)$ can also be interpreted as a normalized tracer concentration, $C(x, t)$. The two terms on the right-hand side term of (17) represent the rates of particles arrival and departure from the location x, respectively. The

equation is nonlocal in both space and in time, and the function $\Phi(x, t)$ in the convolution integrals is often referred to as a memory function. The presence of this convolution implies that the concentration can vary in response (1) to the concentration at distant points, when particles make long jumps and (2) to the concentration at a wide range of previous times, when particles make slow transitions. The actual importance of these two mechanisms is related on the precise form of $\Phi(x, t)$, which in turn depends solely on the pdf $\Psi(x, t)$ according to equation (18).

[15] The GME (17) can be used to derive a partial differential equation that is a more general form of the ADE. The first step is replacing the pdf, $p(x, t)$, with the tracer concentration, $C(x, t)$, and expanding it in a Taylor series. This can be done provided that the concentration, $C(x, t)$, varies smoothly in space. For the sake of convenience, this operation is performed in the Laplace space:

$$\tilde{C}(x', u) \simeq \tilde{C}(x, u) + \frac{\partial \tilde{C}(x, u)}{\partial x}(x' - x) + \frac{1}{2}\frac{\partial^2 \tilde{C}(x, u)}{\partial x^2}(x' - x)^2. \tag{19}$$

[16] After the substitution of this expansion, the Laplace-transformed GME (16) becomes

$$u\tilde{C}(x, u) - \delta(x) = \int_{-\infty}^{+\infty} \tilde{\Phi}(x - x', u)(x' - x)\frac{\partial \tilde{C}(x, u)}{\partial x}\mathrm{d}x' + \int_{-\infty}^{+\infty} \tilde{\Phi}(x - x', u)\frac{(x' - x)^2}{2}\frac{\partial^2 \tilde{C}(x, u)}{\partial x^2}\mathrm{d}x'. \tag{20}$$

[17] In the time domain, this equation is

$$\frac{\partial C(x, t)}{\partial t} = -\int_0^t U^*(t - t')\frac{\partial C(x, t')}{\partial x}\mathrm{d}t' + \int_0^t K^*(t - t')\frac{\partial^2 C(x, t')}{\partial x^2}\mathrm{d}t', \tag{21}$$

where

$$U^*(t) = \int_{-\infty}^{+\infty} x\Phi(x, t)\mathrm{d}x \tag{22}$$

$$K^*(t) = \frac{1}{2}\int_{-\infty}^{+\infty} x^2\Phi(x, t)\mathrm{d}x \tag{23}$$

are an apparent velocity and dispersion coefficient, respectively. Both of these parameters exhibit time-dependent behavior that is related to the jump pdf, $\Psi(x, t)$, as a consequence of equation (18). Thus $\Psi(x, t)$ fully describes the characteristics of the transport process, and equation (21) represents a generalized form of the ADE for arbitrary $\Psi(x, t)$. In fact the ADE represents a special case of equation (21) with $\psi(t)$ as a Dirac delta function, and the TSM is equivalent to this plus a second term containing an exponential distribution. CTRW theory has been used to explain the well-known scaling of dispersivity that has been observed in field experiments of groundwater transport [see *Berkowitz et al.*, 2006, and references therein]. Here we apply this approach to assess the effects of various forms of hyporheic exchange and subsurface structure on downstream solute transport.

[18] Let us now make some reasonable assumptions on the nature of the jump pdf $\Psi(x, t)$ for modeling hyporheic exchange in order to further simplify equation (21). In particular, let us consider the uncoupled jump pdf $\Psi(x, t) = \lambda(x)\psi(t)$. This choice implies that the lengths of the jumps of the particles are independent from their duration. This will often be a good assumption for representing hyporheic exchange because pore water velocities are normally so slow that subsurface transport distances will generally be short relative to in-stream transport distances. The significance of this hypothesis in the context of the hyporheic exchange induced by bedforms is discussed in section 2.2. The assumption of the decoupled pdf allows to rewrite (22)–(23) as

$$U^*(t) = M(t)\cdot U_\Psi \tag{24}$$

$$K^*(t) = M(t)\cdot K_\Psi, \tag{25}$$

where

$$\tilde{M}(u) = u\bar{t}\frac{\tilde{\psi}(u)}{1 - \tilde{\psi}(u)} \tag{26}$$

is a memory function, $\bar{t}$ is a characteristic timescale, and

$$U_\Psi = \frac{1}{\bar{t}}\int_{-\infty}^{+\infty} x\lambda(x)\mathrm{d}x \tag{27}$$

$$K_\Psi = \frac{1}{2\bar{t}}\int_{-\infty}^{+\infty} x^2\lambda(x)\mathrm{d}x \tag{28}$$

are the time-invariant velocity and dispersion coefficient, respectively, over the averaging timescale $\bar{t}$. The choice of the averaging time is then critical and an appropriate choice must be made on the basis of the characteristics of the system of interest. Here a distinction is made on the basis of the fact that transport in the water column is typically much faster than in the subsurface (see section 2.2). With this simplification, the final form of the partial differential equation (21) is then

$$\frac{\partial C(x, t)}{\partial t} = \int_0^t M(t - t')\left[-U_\Psi\frac{\partial C(x, t')}{\partial x} + K_\Psi\frac{\partial^2 C(x, t')}{\partial x^2}\right]\mathrm{d}t'. \tag{29}$$

[19] The expression (29) represents the desired equation for the evolution of the in-stream concentration distribution. Its structure is analogous to the ADE, but with the addition of a convolution integral with the memory function, $M(t)$. This memory function depends uniquely on the time pdf, $\psi(t)$, while the other two parameters, U_Ψ and K_Ψ, are given by the first moments of the length pdf $\lambda(x)$. The use of equation (29) only requires the first two spatial moments of $\lambda(x)$ to be finite, as described by (27)–(28). This is usually expected to be true, as molecular interactions restrict solute

and particle to finite displacement. However, the CTRW approach can also be used with infinite values for the moments of $\lambda(x)$, in which case the spatial derivatives of equation (29) become of fractional order [*Metzler and Klafter*, 2000].

[20] The anomalous, non-Fickian behavior arises because of the convolution integral in (29). The presence of this integral implies that the equation is nonlocal in time whenever the time pdf, $\psi(t)$, includes a wide range of timescales. Memory functions have already been used to model the exchange between streams and hyporheic zones [*Elliott and Brooks*, 1997; *Haggerty et al.*, 2000, 2002; *Marion and Zaramella*, 2005b], and the CTRW approach provides the theoretical tools to relate the anomalous behavior of the solute BTC to the multiple timescales of the flow.

2.2. Application to the Stream Transport of Solutes

[21] The theory of the CTRW is now applied to the case of the transport of solutes in a river reach. Solutes being carried downstream repeatedly enter and leave the hyporheic zone, thereby becoming subject to a much wider range of velocities than found within the stream channel, and resulting in a decrease in their average travel speed. In the CTRW framework, this process can be interpreted as a series of displacements with different traveltimes. The jump pdf $\Psi(x, t)$ that characterize these displacements must be estimated in order to apply the CTRW approach.

[22] Let us focus on the hyporheic exchange induced by the presence of dunes on a streambed composed of moderately permeable sediments such as sand or gravel. In this case there will be a significant flux of water between the surface and subsurface, and yet the fact that there will be a great difference in velocity between the mainstream and the hyporheic zone means that the transport can be described by a decoupled jump pdf, $\Psi(x, t) = \lambda(x)\psi(t)$. Essentially, solutes travel a much shorter distance in the hyporheic zone than in the mainstream during the same amount of time. Thus displacements in the subsurface can be neglected in comparison to those in the river, and the length pdf, $\lambda(x)$, can thus be assumed to depend only on the characteristics of the mainstream flow, without any significant influence due to the exchange with the hyporheic zone. On the other hand, solute traveltime greatly depends on the time spent in the subsurface, and the time pdf, $\psi(t)$, is strongly influenced by the long residence times in the hyporheic zone. In other words, the effect of the hyporheic zone is simply to retain solutes for a certain amount of time. This approach has generally been adopted for analysis of hyporheic exchange [e.g., *Bencala and Walters*, 1983; *Hart*, 1995; *Wörman et al.*, 2002; *Haggerty et al.*, 2002]. The choice of a decoupled jump pdf $\Psi(x, t) = \lambda(x)\psi(t)$ is thus justified, and the problem is reduced to the estimation of the two pdfs $\lambda(x)$ and $\psi(t)$.

[23] The length pdf, $\lambda(x)$, is assumed to be controlled only by the characteristics of the open-channel river flow. The moments of this pdf determine the transport velocity, U_Ψ, and the dispersion coefficient, K_Ψ, through equations (27)–(28). Therefore these two parameters depend only on the velocity profile of the river, as described by the classical theory of [*Taylor*, 1954]. This assumes that the hyporheic exchange does not have a significant effect on the overlying velocity field, which is likely the case for the types of sediments considered here. Therefore the model here can be considered to be semicoupled in the sense that hyporheic exchange is presumed to be induced by the streamflow but to not significantly influence the overlying free-surface flow field. In this case, the transport velocity will be equal to the cross-sectional average river velocity, $U_\Psi = U$, and the dispersion coefficient can be estimated with the traditional expressions [*Fischer et al.*, 1979]. According to Taylor dispersion theory, the ADE only applies after the solute has spread throughout the entire cross section and has completely sampled the transverse velocity profile. The same requirement applies for (29), because in the CTRW it is still required that there has been a sufficient mixing distance for the solute to sample the entire distribution $\lambda(x)$.

[24] The time pdf, $\psi(t)$, represents the distribution of downstream traveltimes t. This distribution includes both the time spent in the main channel and the time spent in the hyporheic zone. The time spent in the channel is described by a pdf, $\psi_0(t)$, whose mean value is the average traveltime in the reach, $\bar{t} = x/U$. This pdf is narrow if compared to the wide range of residence times in the hyporheic zone. Let us now define the exchange rate, Λ, as the probability per unit time that a particle enters the hyporheic zone, and the residence time distribution, $\varphi(t)$, as the pdf of traveltimes in the subsurface. Both quantities can be obtained from the physically based models of hyporheic exchange [e.g., *Elliott and Brooks*, 1997; *Packman et al.*, 2000; *Packman and Brooks*, 2001; *Boano et al.*, 2007; *Cardenas*, 2007]. The total time spent in the hyporheic zone also depends on the frequency with which solutes enter the subsurface. The probability that a tracer particle enters the hyporheic zone a certain number of times can be described by a Poisson process with a probability per unit time Λ. Each time the particle enters the hyporheic zone, it is retained for a time that is randomly extracted from $\varphi(t)$. In their work, *Margolin et al.* [2003] have used the same approach to model adsorption/desorption behavior, and have derived an analytical expression for the overall time pdf, $\psi(t)$. In Laplace space, this equation reads

$$\tilde{\psi}(u) = \tilde{\psi}_0[u + \Lambda - \Lambda\tilde{\varphi}(u)]. \tag{30}$$

[25] Equation (30) has also been successfully applied by *Cortis et al.* [2006] to obtain a generalized CTRW filtration model for colloid transport in porous media involving multiple deposition/resuspension events. This expression links the overall time pdf, $\psi(t)$, with the characteristics of hyporheic exchange, Λ and $\varphi(t)$. When the exchange rate $\Lambda \to 0$, only a small fraction of the solute mass enters the hyporheic zone and the overall time pdf reduces to the one for in-stream transport, $\tilde{\psi}(u) \equiv \tilde{\psi}_0(u)$. On the other hand, when $\Lambda > 0$, since the residence time pdf $\varphi(t)$ is usually much wider than the $\psi_0(t)$, the effect of the hyporheic exchange is to broaden the range of timescales that characterize the transport of solutes. It should be noted here that a wide $\psi(t)$ is exactly the cause of non-Fickian transport [*Berkowitz et al.*, 2006].

[26] Once the function $\tilde{\psi}(u)$ is known, it can be introduced into equation (26) to derive the memory function, $M(t)$. This function, together with the transport velocity, U_Ψ, and the dispersion coefficient, K_Ψ, completes the set of the

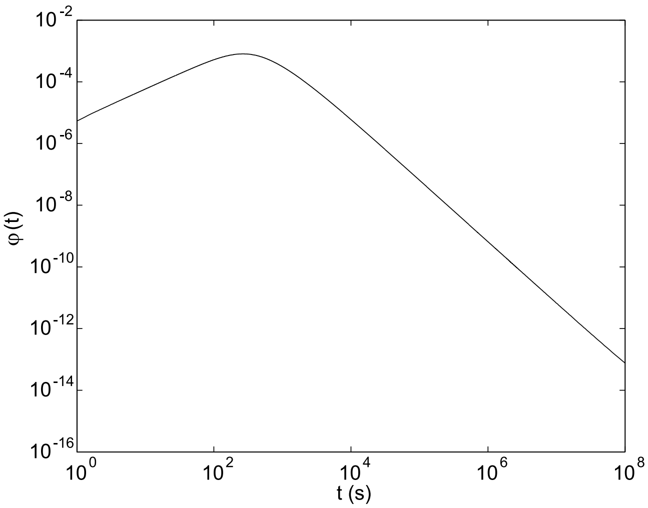

Figure 1. Residence time distribution for a single travel in the hyporheic zone.

parameters required to apply the generalized form of the ADE, equation (29).

3. Examples

[27] Several examples are used to illustrate the application of the CTRW to assess the effects of hyporheic exchange on downstream solute transport in rivers. First, the case of a river with bedforms of regular geometry is simulated, and then the additional complexities arising from irregular bedforms and heterogeneous sediments are considered in order to show how these aspects can easily be incorporated in the CTRW approach.

3.1. Regular Bedforms

[28] Simulations are performed for a uniform stream with depth $d = 0.5$ m, mean velocity $U = 0.5$ m/s, and dispersion coefficient $K = 11$ m^2/s. The river bed is considered to be covered with dunes with constant height, $H = 0.1$ m, and with a wavelength-to-height ratio $L/H = 2\pi$. The bed sediments are considered to be homogeneous and isotropic with a hydraulic conductivity and porosity of $K = 5 \cdot 10^{-3}$ m/s and $n = 0.3$, respectively. These values are representative of a mixture of sand and gravel. The application of the advective pumping model [*Elliott and Brooks*, 1997] to this case reveals that the exchange flux per unit bed area is $q = 5 \cdot 10^{-2}$ L/(s m^2), and the subsurface residence time distribution, $\varphi(t)$, has the form shown in Figure 1. Note that the advective hyporheic exchange induced by bedforms involves a wide range of subsurface traveltimes. In fact the residence time distribution shows classic ''long tail'' behavior, decaying as a power law, $\varphi(t) \approx t^{-2}$. The exchange rate, Λ, is evaluated as the ratio between the hyporheic flux exchanged per unit bed area and the volume of the water column over the same area, that is, $\Lambda = q/d = 9 \cdot 10^{-5}$ s^{-1}, where d is the stream depth.

[29] The injection of a conservative tracer at a constant rate for two hours is simulated, and the resulting concentration distribution is evaluated $x = 1$ km downstream from the source. This distance is sufficient to provide complete mixing across the river cross section, as required for the application of the ADE as well as for equation (29). The characteristic traveltime to traverse the reach is $\bar{t} = x/U = 2000$ s. The in-stream traveltime distribution is represented with an exponential pdf having a mean value $\bar{t}$, $\psi_0(t) = \exp(-t/\bar{t})/\bar{t}$. It can be shown that the exact shape of $\psi_0(t)$ does not influence the results, provided that the width of $\psi_0(t)$ is much smaller than that of $\varphi(t)$. Hence any short-tailed distribution for $\psi_0(t)$ having an appropriate average can be adopted. It should be noted that the introduction of an exponential pdf in equation (26) leads to $M(t) = \delta(t)$, which would reduce equation (29) to the ADE in the absence of hyporheic exchange.

[30] The length of the reach is much longer than the bedform wavelength, providing the opportunity for solutes to repeatedly enter the hyporheic zone as they traverse the reach. The overall time pdf, $\psi(t)$, is obtained using equation (30), and the consequent memory function, $M(t)$, is evaluated by means of equation (26). It is thus possible to apply the CTRW equation (29) to the hyporheic exchange problem using the solution method described by *Cortis and Berkowitz* [2005]. The resulting in-stream concentration distribution is presented in Figure 2a, where the

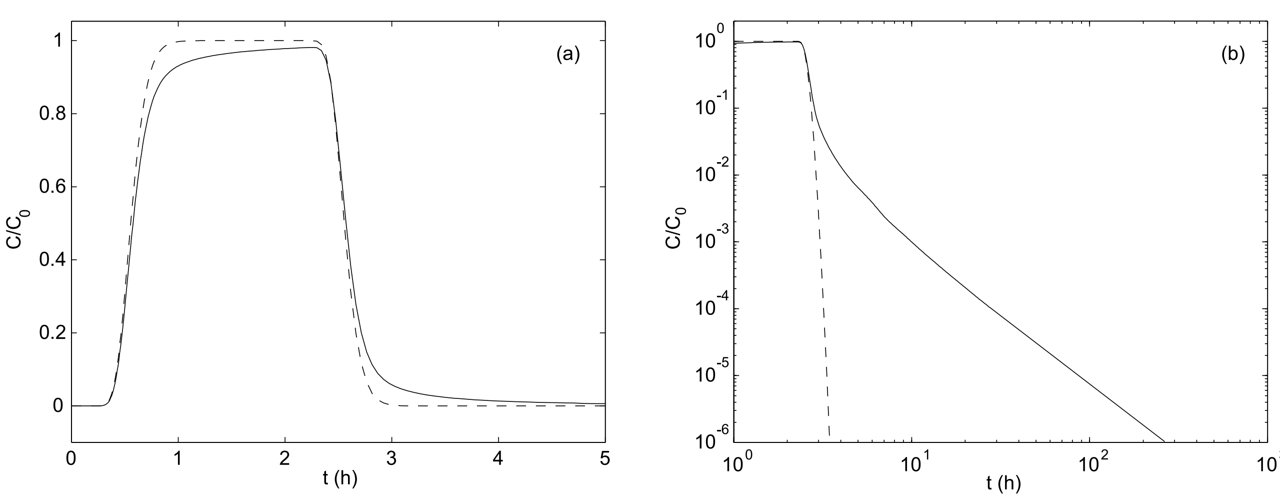

Figure 2. In-stream solute concentration distribution 1 km downstream of the injection point, obtained with the ADE (dashed line) and the CTRW (solid line). (a) Complete curve and (b) detail of the tail.

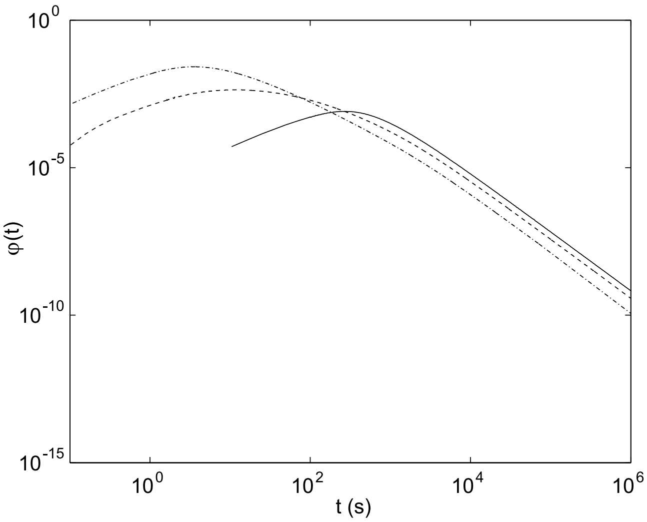

Figure 3. Comparison between the hyporheic residence time distribution for a single bedform (solid line) and for a distribution of dune heights with $\sigma_H/\bar{H} = 1$ (dashed line) and $\sigma_H/\bar{H} = 5$ (dash-dotted line).

breakthrough curve obtained with the ADE is also shown for comparison. Note that solute concentrations have been normalized with the maximum concentration, C_0.

[31] The comparison between the two curves in Figure 2a shows that hyporheic exchange produces a delay in the arrival of solutes and a longer tail in the breakthrough curve. The tailing behavior can more easily be seen when plotted on a logarithmic scale, Figure 2b. These effects are due to the long retention times associated with the hyporheic exchange, and the results agree with the observations from field tests and predictions of other models [*Bencala and Walters*, 1983; *Hart*, 1995; *Wörman et al.*, 2002]. In particular, the kind of decay agrees with the solute injection results obtained by *Haggerty et al.* [2002], who observed that hyporheic exchange gives rise to breakthrough curves with a power law tail. It should be stressed that the precise shape of the BTC, e.g., the power law exponent of the tail, depends on the exact type of residence time pdf, $\varphi(t)$.

[32] A bed of infinite depth is here considered, but the model can easily be extended to include a shallow impermeable layer [*Packman et al.*, 2000; *Zaramella et al.*, 2003]. The introduction of an impermeable layer would actually introduce a cutoff time, T, in the residence time pdf. In this case the BTC tail would show a power law behavior only for $t < T$, and then it would switch back again to the classical, faster decay (as for the ADE). This transition between anomalous and normal behavior can be predicted by the CTRW model [see *Dentz et al.*, 2004, Figure 14].

3.2. Distribution of Bedform Sizes

[33] The model is now applied to a river whose bed is covered with a series of bedforms of different sizes. The range of bedform heights is described by a pdf, $p(H)$, while the wavelength-to-height ratio is considered to remain constant. The exchange induced by each bedform is assumed to be independent, with each one inducing an exchange flux that depends on its height and on the stream characteristics [*Elliott and Brooks*, 1997; *Boano et al.*, 2007]

$$q = \frac{kKh_0}{\pi}, \tag{31}$$

where $k = 2\pi/L$ is the dune wave number, L is the dune wavelength, and

$$h_0 = 0.28\frac{U^2}{2g}\left(\frac{H/d}{0.34}\right)^m \qquad m = \begin{cases} 3/8 \ H/d < 0.34 \\ 3/2 \ H/d > 0.34. \end{cases} \tag{32}$$

[34] Because the exchange flux varies with bedform height, solutes have different probabilities of entering the different bedforms. The pdf of bedform heights, $p(H)$, can be converted into a pdf of hyporheic fluxes

$$p(q) = p(H)\cdot\left(\frac{\mathrm{d}q}{\mathrm{d}H}\right)^{-1}, \tag{33}$$

where the derivative dq/dH can is obtained from (31)–(32).

[35] It is now possible to define a flux-averaged residence time distribution as

$$\varphi(t) = \frac{\int_0^{+\infty} q\,\varphi(t|q)p(q)\mathrm{d}q}{\bar{q}}, \tag{34}$$

where $\varphi(t|q)$ is the residence time pdf for a bedform that induces the exchange flux q, and $\bar{q} = \int_0^{+\infty} q\,p(q)\mathrm{d}q$ is the average exchange flux. The resulting average residence time pdf, $\varphi(t)$, and the average exchange rate, $\Lambda = \bar{q}/d$, can then be introduced in equation (29) to evaluate the breakthrough curve at the end of the reach.

[36] In the present example, a lognormal pdf, $p(H)$ is adopted to describe the distribution of bedform heights. The mean bedform height is taken to be identical to that used in the previous example, $\bar{H} = 0.1$ m. The standard deviation, σ_H, is varied to investigate the importance of the irregularities of the bedforms on the breakthrough curve. In order to consider a range of bedform sizes that is physically reasonable, the pdf has been cut off between a minimum and maximum size, $H_1 = 0.5$ cm and $H_2 = 30$ cm, respectively. The values of all other parameters are the same as used in the previous example (see section 3.1).

[37] The average residence time distributions, $\varphi(t)$, for different values of the ratio $\sigma_H/\bar{H}$ are shown in Figure 3. The case of regular bedforms is also included for comparison. Figure 3 shows how the variance of the average residence time pdf, $\varphi(t)$, increases when the streambed is covered by bedforms with different sizes. Because of the skewed shape of the lognormal pdf $p(H)$, smaller bedforms (and thus shorter retention times) become more prevalent when the coefficient of variation $\sigma_H/\bar{H}$ increases.

[38] The effects of the different distributions of dune heights on the breakthrough curve are shown in Figure 4a. The breakthrough curves show increasing deviation from the regular bedform case for increasing coefficient of variation of the bedform size distribution, $\sigma_H/\bar{H}$. However, these differences are not very large, because the range of residence times produced by the average dune size is

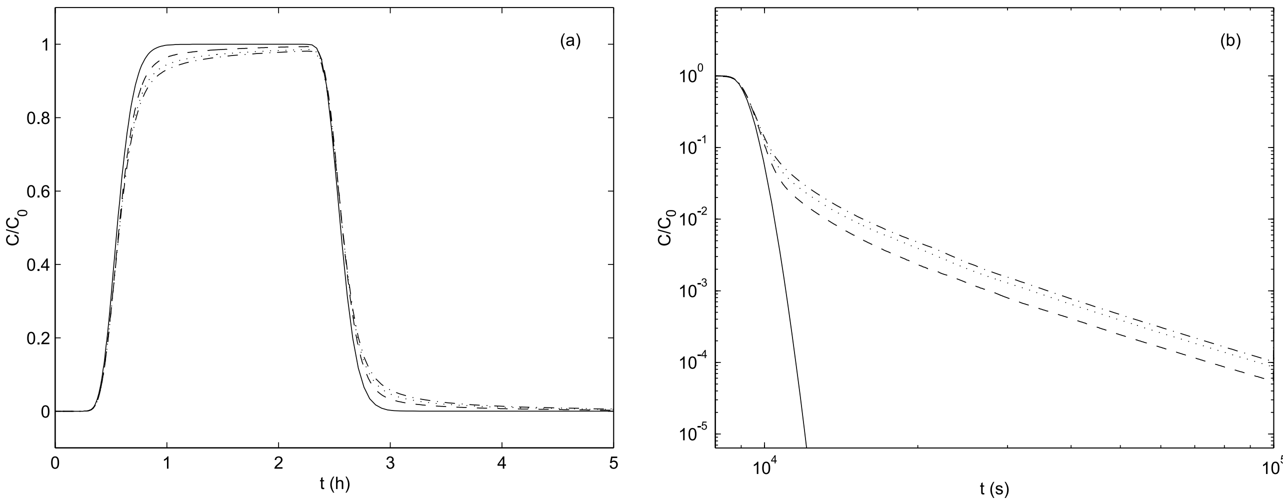

Figure 4. Comparison of the in-stream concentrations 1 km downstream of the injection point for the case of no hyporheic exchange (solid line), regular bedforms (dash-dotted line), and a distribution of dune heights with $\sigma_H/\bar{H}$ = 1 (dotted line) and $\sigma_H/\bar{H}$ = 5 (dashed line). (a) Complete curve and (b) detail of the tail.

already so wide that it is not greatly modified by the presence of different bedform sizes. This behavior indicates that the mean bedform height, $\bar{H}$, will often provide a reasonable estimate of the hyporheic exchange, as previously suggested by *Packman et al.* [2000]. The breakthrough curves also become increasingly closer to the ADE case with higher $\sigma_H/\bar{H}$. This behavior can be more clearly observed looking at the tails of the concentration curves in Figure 4b. This is due to the increasing importance of the shorter exchange timescales and the resulting faster release of solutes to the mainstream. This behavior depends on the shape of the specific distribution that has been assumed for $p(H)$.

3.3. Small-Scale Heterogeneities

[39] In the previous examples, sediments were considered to be homogeneous, but here we investigate the effects of sediment heterogeneity. We focus specifically on the case of heterogeneities whose correlation length is much smaller than the bedform wavelength. In this case, the shape of the hyporheic flow paths is not significantly altered by the variations of the hydraulic conductivity, but the heterogeneity does influence the traveltime along each flow path.

[40] The residence time pdf in the hyporheic zone, $\varphi(t)$, is thus given by

$$\varphi(t) = \int_0^t \varphi_{\bar{K}}(t-\tau)\phi(\tau)\mathrm{d}\tau, \tag{35}$$

where $\varphi_{\bar{K}}(t)$ is the residence time pdf for a homogenous hyporheic zone with mean hydraulic conductivity $\bar{K}$, and $\phi(t)$ is the pdf of the delay times due to the variation of hydraulic conductivity around the mean.

[41] Again we consider a river with the same characteristics as in the example of section 3.1, but with heterogeneous sediments.

[42] A number of functions have been proposed to model the heterogeneities of sand and gravel sediments [*Berkowitz et al.*, 2006]. The type of model function for $\phi(t)$ should be chosen according to the available knowledge of the properties of the sediments. In this analysis, a truncated power law (TPL) expression has been adopted

$$\phi(t) = \frac{1}{t_2\,\Gamma(-\beta, t_1/t_2)} \frac{\mathrm{e}^{-(t+t_1)/t_2}}{(1+t/t_1)^{1+\beta}}, \tag{36}$$

where t_1 and t_2 are two cutoff times, $\Gamma(a,\ x)$ is the incomplete Gamma function [*Abramowitz and Stegun*, 1965], and β is an exponent that is related the degree of heterogeneity of the sediments. The TPL displays a power law behavior, $\phi(t) \approx t^{-1-\beta}$, for $t_1 < t < t_2$, and it switches to an exponential decay for $t > t_2$. A homogeneous medium is characterized by $\beta = 2$, and lower values of β are typical of more heterogeneous systems [*Cortis and Berkowitz*, 2004; *Jiménez-Hornero et al.*, 2005]. The transition to the exponential behavior occurs when the length of travel is much longer than the correlation scale of the sediment structure. In this case, the flow field has adequately sampled the entire distribution of hydraulic conductivity, and its motion is then the same as in an equivalent homogeneous medium.

[43] This indicates that the correlation length scale of the heterogeneities, ℓ, should be much smaller than the dune wavelength in order to avoid altering the shape of the flow paths. Since the dune wavelength is about 60 cm, it has been assumed that ℓ is on the order of millimeters. The characteristic pore fluid velocity, $u_0 = kKh_0/\theta$, is of the order of 10^{-4} m/s at the streambed surface, and it decreases exponentially with the depth [*Elliott and Brooks*, 1997]. Therefore it is assumed that $t_1 > \ell/u_0 \approx 10$ s. Similarly, the effects of heterogeneity will disappear after a travel distance of $\approx$100 ℓ, or $t_2 \approx 10^3$ s. Because little information is available to constrain the choice of the CTRW variables, we perform a parametric study on the influence of the values of t_1, t_2, and β, and thus of the shape of $\phi(t)$.

[44] The effect of sediment heterogeneity on the overall residence time pdf $\varphi(t)$ is illustrated in Figure 5. Figure 5 shows how the residence time pdf for the homogeneous bed,

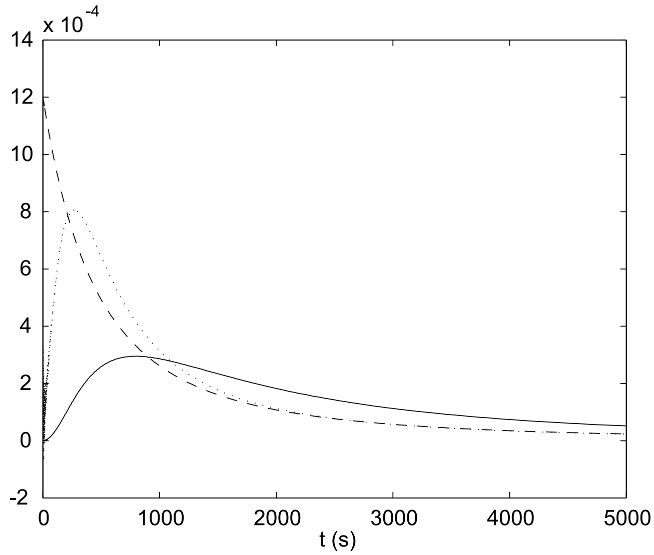

Figure 5. Residence time distribution for a heterogeneous bed $\varphi(t)$ (solid line), resulting from the convolution of the residence time pdf for a homogeneous bed $\varphi_{\bar{K}}(t)$ (dotted line) with a delay time pdf for heterogeneity $\phi(t)$ in the form of a TPL with $t_1 = 10^3$ s, $t_2 = 10^6$ s, and $\beta = 1.2$ (dashed line).

$\varphi_{\bar{K}}(t)$, is transformed because of the presence of heterogeneities characterized by the delay time pdf, $\phi(t)$. In this example $\phi(t)$ is a TPL with $t_1 = 10^3$ s, $t_2 = 10^6$ s, and $\beta = 1.2$. It can be observed that the range of retention times, represented by the length of the tail of $\varphi(t)$, is broadened by the introduction of the heterogeneities. This happens whenever the characteristic timescale of $\phi(t)$ approaches that of $\varphi_{\bar{K}}(t)$.

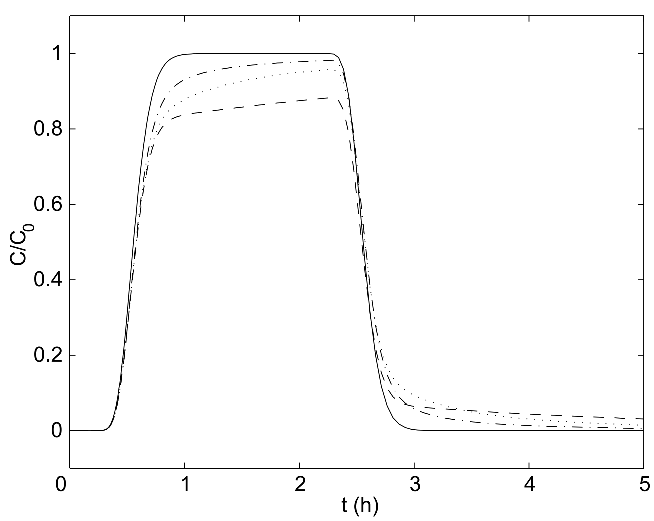

Figure 6. Comparison of in-stream concentration distributions 1 km downstream of the injection point for the cases of no hyporheic exchange (solid line), homogeneous sediments (dash-dotted line), and heterogeneous sediments characterized by a TPL with $t_1 = 10^3$ s (dotted line) and $t_1 = 10^4$ s (dashed line); $t_2 = 10^6$ s and $\beta = 1.2$ in both cases.

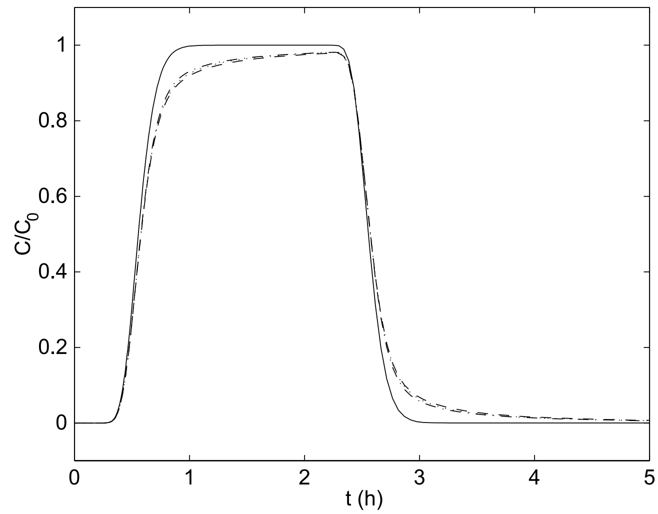

Figure 7. Comparison of the in-stream concentration distributions 1 km downstream of the injection point for the cases of no hyporheic exchange (solid line), homogeneous sediments (dash-dotted line), and heterogeneous sediments characterized by a TPL with $t_2 = 10^3$ s (dotted line) and $t_2 = 10^5$ s (dashed line); $t_1 = 10^2$ s and $\beta = 1.2$ in both cases.

[45] The effect of t_1 is illustrated in Figure 6, for the case of $t_2 = 10^6$ s and $\beta = 1.2$. The chosen value of β is representative of weak heterogeneity, and the value of t_2 is higher than the total duration of the observations. The time to peak and extent of the tail both increase as t_1 increases. This indicates that subsurface heterogeneities can increase the retention of the solutes in the hyporheic zone, and amplify the effect of the hyporheic exchange on downstream solute transport.

[46] Figures 7 and 8 show the influence of different values of t_2 and β, respectively. While t_2 has a negligible influence, β significantly modifies the shape of the in-stream breakthrough curve. The values $\beta = 1.2$ and $\beta = 0.6$ adopted in Figure 8 are representative of weak and strong heterogeneities, respectively, so the deviation from the homogeneous case increases as β decreases.

4. Conclusions

[47] The flow continuum in rivers includes both the overlying free-surface flow and underlying pore fluid flow, and therefore encompasses an extremely wide spectrum of advective velocities. The entire range of velocities influences solute transport in river corridors, but established methods for assessing downstream solute transport typically consider only a limited range of transport timescales, either those associated with the open-channel velocity distributions that give rise to classic in-stream dispersion [*Taylor*, 1954; *Fischer et al.*, 1979], or the somewhat wider range of timescales associated with first-order transient storage behavior [e.g., *Bencala and Walters*, 1983; *Packman and Bencala*, 2000]. Here we have presented an improved modeling approach for representing the multitude of timescales found in rivers on the basis of continuous time random walk theory, which envisions transport as a stochastic process involving a series of transport steps having

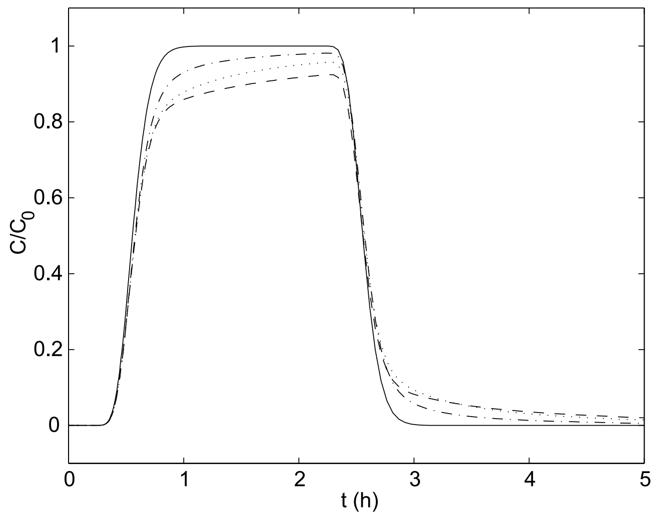

Figure 8. Comparison of the in-stream concentration distributions 1 km downstream of the injection point for the cases of no hyporheic exchange (solid line), homogeneous sediments (dash-dotted line), and heterogeneous sediments characterized by a TPL with $\beta = 1.2$ (dotted line) and $\beta = 0.6$ (dashed line); $t_1 = 10^3$ s and $t_2 = 10^6$ s in both cases.

different lengths and durations. The CTRW model allows the evolution of a solute concentration distribution to be described with a single partial differential equation that includes the effects of both in-stream and subsurface transport. This calculation involves a convolution of the transport term with a memory function that can represent a very wide range of transport timescales. In addition to being able to represent standard advection-dispersion and transient storage behavior, the governing equation can also represent transport behavior that is nonlocal in time when the memory function has a sufficiently wide distribution (i.e., a long tail). The CTRW approach is thus a highly suitable theoretical framework for the analysis of transport problems in rivers, and it offers very particular advantages for modeling the effects of surface-subsurface interactions on downstream transport.

[48] The major advantage of the proposed model is that it allows to predict the in-stream breakthrough curves without the need for parameter calibration through curve fitting. The values of the CTRW model parameters can be obtained from the upscaling of the local residence time pdfs. The upscaling approach requires making measurements in order to characterize both the boundary morphology and subsurface properties, e.g., hydraulic conductivity and bedform geometry. Further confidence in the model performance can be obtained by directly measuring solute concentrations in the subsurface, but this is already recommended [*Harvey and Wagner*, 2000]. Thus a wide variety of different transport and storage processes at different scales can be implemented in the CTRW approach, provided that the associated exchange fluxes and residence timescales can be characterized. The combined action of exchange induced by different processes over a wide range of spatial scales results in very wide residence time pdfs [*Wörman et al.*, 2007], and tend to produce power law tailed breakthrough curves [*Haggerty et al.*, 2002; *Kirchner et al.*, 2000]. The precise shape of the breakthrough curve, as well as the slope of its tail, therefore depends on the overall effect of all the involved transport and retention processes.

[49] The capability of the model was illustrated by means of a series of examples. Simulations of advective hyporheic exchange induced by bedforms clearly demonstrate that the wide range of timescales associated with advective pore water transport produces strong asymmetry (long tails) in in-stream breakthrough curves. This anomalous behavior arises whenever the waiting time distribution is wider than the typical advective timescale. The CTRW framework also provides the capability to assess additional complexities such as spatial variability in bedform size and local heterogeneity in the bed sediments. These and other similar effects can be represented by convolving suitable descriptions of these behaviors into the transition probability distribution that defines the memory function. Including a reasonable distribution of bedform sizes in the simulations did not have a substantial effect on the range of exchange timescales because the variability in bedform geometry was much less than the extent of variability in pore fluid velocity under a single bedform. This result indicates that net downstream transport should often be able to be predicted well using measures of average bed roughness, as suggested previously by *Packman et al.* [2000]. Subsurface heterogeneity was found to have a much more significant effect on solute transport because the delay times associated with regions of low permeability can greatly extend subsurface residence time distributions.

[50] Here parameter combinations typical of lowland, sand bed rivers have been used. These cases are favorable for initial consideration because the permeability of sands limits pore water velocities and thereby allows the transport behavior to be analyzed in a semicoupled fashion; that is, the occurrence of hyporheic exchange does not have an appreciable effect on the overlying stream flow, and also transport distances in the subsurface are insignificant relative to those in the free-surface flow. Further, sand beds tend to be only weakly heterogeneous, which allows the effects of heterogeneity to be completely represented by means of an independent delay time distribution. In other words, in this case heterogeneity does not change the pattern of pore water flow, but only broadens the time distribution for travel along each flow path. Coarser and more heterogeneous sediments are expected to show more complex behavior requiring more detailed analysis of the coupling between the overlying flow, the pore flow field, and the sediment structure. This can be done by means of suitable numerical models [e.g., *Salehin et al.*, 2004; *Saenger et al.*, 2005], but it is generally difficult to obtain sufficient information on subsurface structure and transport in coarse streambed sediments to support detailed analysis of these types of streams.

[51] It is important to note that the effects of surface-subsurface interactions are completely parameterized in the CTRW model in terms of the boundary exchange flux and the subsurface residence time distribution. Both of these quantities can be estimated as a function of the overlying flow conditions and streambed morphology using a variety of physically based models that have been developed in the past decade, and they can also be measured in situ [*Harvey and Wagner*, 2000; *Wörman et al.*, 2002]. The CTRW

approach can also be easily extended to consider other mechanisms of hyporheic exchange and in-stream storage, as soon as sufficient information becomes available to allow adequate parameterization of these processes. Finally, the CTRW approach has also been successfully applied to represent the effects of various local-scale biological and physicochemical interactions between mobile substances and stationary solid phases, such as adsorption/desorption of contaminants and attachment/detachment of pathogens [*Margolin et al.*, 2003; *Cortis et al.*, 2006]. These local-scale processes can be included in a reach-scale CTRW model in exactly the same manner that the effects of local-scale heterogeneities were incorporated here. The model thus provides an extremely flexible framework for analyzing the transport of a wide variety of substances in streams and rivers.

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References

Abramowitz, M., and I. A. Stegun (1965), *Handbook of Mathematical Functions*, Dover, New York.

Bencala, K. E., and R. A. Walters (1983), Simulation of solute transport in a mountain pool-and-riffle stream: A transient storage model, *Water Resour. Res.*, *19*(3), 718–724.

Berkowitz, B., A. Cortis, M. Dentz, and H. Scher (2006), Modeling non-Fickian transport in geological formations as a continuous time random walk, *Rev. Geophys.*, *44*, RG2003, doi:10.1029/2005RG000178.

Boano, F., R. Revelli, and L. Ridolfi (2007), Bedform-induced hyporheic exchange with unsteady flows, *Adv. Water Resour.*, *30*(1), 148–156.

Boulton, A., S. Findlay, P. Marmonier, E. Stanley, and H. Valett (1998), The functional significance of the hyporeic zone in streams and rivers, *Annu. Rev. Ecol. Syst.*, *29*, 59–81.

Broshears, R., K. Bencala, B. Kimball, and D. McKnight (1993), Tracer-dilution experiments and solute-transport simulations for a mountain stream, Saint Keving Gulch, Colorado, *U.S. Geol. Surv. Tech. Water Resour Invest. Rep., 92-4081*.

Brunke, M., and T. Gonser (1997), The ecological significance of exchange processes between rivers and groundwater, *Freshwater Biol.*, *37*, 1–33, doi:10.1046/j.1365-2427.1997.00143.x.

Cardenas, M. (2007), Potential contribution of topography-driven regional groundwater flow to fractal stream chemistry: Residence time distribution analysis of Tóth flow, *Geophys. Res. Lett.*, *34*, L05403, doi:10.1029/2006GL029126.

Castro, N. M., and G. M. Hornberger (1991), Surface-subsurface water interactions in an alluviated mountain stream channel, *Water Resour. Res.*, *27*(7), 1613–1621.

Cortis, A., and B. Berkowitz (2004), Anomalous transport in "classical" soil and sand columns, *Soil Sci. Soc. Am. J.*, *68*(5), 1539–1548.

Cortis, A., and B. Berkowitz (2005), Computing "anomalous" contaminant transport in porous media: The CTRW MATLAB toolbox, *Ground Water*, *43*(6), 947–950.

Cortis, A., T. Harter, L. L. Hou, E. R. Atwill, A. I. Packman, and P. G. Green (2006), Transport of Cryptosporidium parvum in porous media: Long-term elution experiments and continuous time random walk filtration modeling, *Water Resour. Res.*, *42*(12), W12S13, doi:10.1029/2006WR004897.

Dentz, M., A. Cortis, H. Scher, and B. Berkowitz (2004), Time behavior of solute transport in heterogeneous media: Transition from anomalous to normal transport, *Adv. Water Resour.*, *27*(2), 155–173.

Elliott, A. H., and N. H. Brooks (1997), Transfer of nonsorbing solutes to a streambed with bed forms: Theory, *Water Resour. Res.*, *33*(1), 123–136.

Fernald, A. G., P. Wigington Jr., and D. H. Landers (2001), Transient storage and hyporheic flow along the Willamette River, Oregon: Field measurements and model estimates, *Water Resour. Res.*, *37*(6), 1681–1694.

Fischer, H., J. Imberger, E. List, R. Koh, and N. Brooks (1979), *Mixing in Inland and Coastal Waters*, Academic Press, New York.

Haggerty, R., S. A. McKenna, and L. C. Meigs (2000), On the late-time behavior of tracer test breakthrough curves, *Water Resour. Res.*, *36*(12), 3467–3479.

Haggerty, R., S. M. Wondzell, and M. A. Johnson (2002), Power-law residence time distribution in the hyporheic zone of a 2nd-order mountain stream, *Geophys. Res. Lett.*, *29*(13), 1640, doi:10.1029/2002GL014743.

Hancock, P., A. Boulton, and W. Humphreys (2005), Aquifers and hyporheic zones: Towards an ecological understanding of groundwater, *Hydrogeol. J.*, *13*, 98–111.

Hart, D. R. (1995), Parameter estimation and stochastic interpretation of the transient storage model for solute transport in streams, *Water Resour. Res.*, *31*(2), 323–328.

Harvey, J. W., and C. C. Fuller (1998), Effect of enhanced manganese oxidation in the hyporheic zone on basin-scale geochemical mass balance, *Water Resour. Res.*, *34*(4), 623–636.

Harvey, J., and B. Wagner (2000), Quantifying hydrologic interactions between streams and their subsurface hyporheic zones, in *Streams and Ground Waters*, *Aquat. Ecol. Ser.*, edited by J. B. Jones and P. J. Mulholland, pp. 3–44, Academic, San Diego, Calif.

Harvey, J. W., B. J. Wagner, and K. E. Bencala (1996), Evaluating the reliability of the stream tracer approach to characterize stream-subsurface water exchange, *Water Resour. Res.*, *32*(8), 2444–2451.

Jiménez-Hornero, F. J., J. V. Giráldez, A. Laguna, and Y. Pachepsky (2005), Continuous time random walks for analyzing the transport of a passive tracer in a single fissure, *Water Resour. Res.*, *41*(4), W04009, doi:10.1029/2004WR003852.

Jones, J. B., and P. J. Mulholland (Eds.) (2000), *Streams and Ground Waters*, Academic, San Diego, Calif.

Kirchner, J. W., X. H. Feng, and C. Neal (2000), Fractal stream chemistry and its implications for contaminant transport in catchments, *Nature*, *403*(6769), 524–527.

Klafter, J., and R. Silbey (1980), Derivation of the continuous-time random walk equation, *Phys. Rev. Lett.*, *44*(2), 55–58.

Margolin, G., M. Dentz, and B. Berkowitz (2003), Continuous time random walk and multirate mass transfer modeling of sorption, *Chem. Phys.*, *295*, 71–80.

Marion, A., and M. Zaramella (2005a), Diffusive behavior of bedform-induced hyporheic exchange in rivers, *J. Environ. Eng.*, *131*(9), 1260–1266.

Marion, A., and M. Zaramella (2005b), A residence time model for stream-subsurface exchange of contaminants, *Acta Geophys. Pol.*, *53*(4), 527–538.

Marion, A., M. Zaramella, and A. I. Packman (2003), Parameter estimation of the transient storage model for stream-subsurface exchange, *J. Environ. Eng.*, *129*(5), 456–463.

Metzler, R., and J. Klafter (2000), The random walk's guide to anomalous diffusion: A frational dynamics approach, *Phys. Rep.*, *339*, 1–77.

Montroll, E. W., and G. H. Weiss (1965), Random walks on lattices. II, *J. Math. Phys.*, *6*(2), 167–181.

Nordin, C. F. J., and B. M. Troutman (1980), Longitudinal dispersion in rivers: The persistence of skewness in observed data, *Water Resour. Res.*, *16*(1), 123–128.

Packman, A., and K. Bencala (2000), Modeling surface-subsurface hydrological interactions, in *Streams and Ground Waters*, *Aquat. Ecol. Ser.*, edited by J. B. Jones and P. J. Mulholland, pp. 45–80, Academic, San Diego, Calif.

Packman, A. I., and N. H. Brooks (2001), Hyporheic exchange of solutes and colloids with moving bed forms, *Water Resour. Res.*, *37*(10), 2591–2605.

Packman, A. I., N. H. Brooks, and J. J. Morgan (2000), A physicochemical model for colloid exchange between a stream and a sand streambed with bed forms, *Water Resour. Res.*, *36*(8), 2351–2362.

Saenger, N., P. K. Kitanidis, and R. L. Street (2005), A numerical study of surface-subsurface exchange processes at a riffle-pool pair in the Lahn River, Germany, *Water Resour. Res.*, *41*, W12424, doi:10.1029/2004WR003875.

Salehin, M., A. I. Packman, and M. Paradis (2004), Hyporheic exchange with heterogeneous streambeds: Laboratory experiments and modeling, *Water Resour. Res.*, *40*, W11504, doi:10.1029/2003WR002567.

Scher, H., and M. Lax (1973), Stochastic transport in a disordered solid, I. Theory, *Phys. Rev. B*, *7*, 4491–4502.

Schmid, B. H. (2002), Persistence of skewness in longitudinal dispersion data: Can the dead zone model explain after all?, *J. Hydraul. Eng.*, *128*(9), 848–854.

Schnoor, J. L. (1996), *Environmental Modeling*, John Wiley, New York.
Taylor, G. (1954), The dispersion of matter in turbulent flow through a pipe, *Proc. R. Soc. London, Ser. A*, *223*, 446–468.
Thibodeaux, L. J., and J. D. Boyle (1987), Bedform-generated convective transport in bottom sediment, *Nature*, *325*(6102), 341–343.
Thomas, S. A., H. M. Valett, J. R. Webster, and P. J. Mulholland (2003), A regression approach to estimating reactive solute uptake in advective and transient storage zones of stream ecosystems, *Adv. Water Resour.*, *26*, 965–976.
Wörman, A., A. I. Packman, H. Johansson, and K. Jonsson (2002), Effect of flow-induced exchange in hyporheic zones on logitudinal transport of solutes in streams and rivers, *Water Resour. Res.*, *38*(1), 1001, doi:10.1029/2001WR000769.
Wörman, A., A. Packman, L. Marklund, J. Harvey, and S. Stone (2007), Fractal topography and subsurface water flows from fluvial bedforms to the continental shield, *Geophys. Res. Lett.*, *34*, L07402, doi:10.1029/2007GL029426.
Yotsukura, N., H. B. Fischer, and W. W. Sayre (1970), Measurement of mixing characteristics of the Missouri River between Sioux City, Iowa, and Plattsmouth, Nebraska, *U.S. Geol. Surv. Water Supply Pap., 1899-G*.
Zaramella, M., A. I. Packman, and A. Marion (2003), Application of the transient storage model to analyze advective hyporheic exchange with deep and shallow sediments, *Water Resour. Res.*, *39*(7), 1198, doi:10.1029/2002WR001344.

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